A New Family of Ionic Liquids 1-amino-3-alkyl-1,2,3-triazolium nitrates.

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A new class of ionic liquids based upon 1-amino-3-alkyl-1,2,3-triazolium nitrates (alkyl = methyl, ethyl, n-propyl, 2-propenyl, and n-butyl) have been synthesized and characterized by vibrational spectra, multinuclear NMR, elemental analysis, and DSC studies. A single crystal x-ray study was carried out for 1-amino-3-methyl-1,2,3-triazolium nitrate and the details will be presented.

Introduction

The most accepted definition of an ionic liquid is a salt with melting point below 100°C.[1-6] Ionic liquids attract increasing attention among academic and industrial chemists for their unique properties. Their very low and often non-detectable vapor pressure, long liquidous range, high thermal and electrical conductivity as well as high thermal stability, allow researchers to use them as electrolytes, solvents, and in catalytic processes. Tetralkyl(ammonium) and phosphonium, 1,3-dialkyl-imidazolium and 1-alkyl-pyridinium salts are amongst the most widely studied. Most research efforts have relied

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **JUL 2004**	2. REPORT TYPE	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **A New Family of Ionic Liquids 1-Amino-1,2,3-Triazolium Nitrates**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Greg Kaplan; Greg Drake; Leslie Hall; Tommy Hawkins; Joann Larue**	5d. PROJECT NUMBER **1011**
	5e. TASK NUMBER **0046**
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **ERC, Inc.,AFRL/PRS,10 E. Saturn Blvd.,Edwards AFB,CA,93524-7680**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
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15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**20**	

heavily on commercially available 1,3-dialkyl-imidazolium based ionic liquids.[1-6] Industrial applications of imidazolium based ionic liquids have been recently reported.[6,7] The shape and size of the alkyl side chains on the imidazolium cation as well as charge delocalization over the highly asymmetric ion is believed to be responsible for the poor crystal lattice packing, thus resulting in low melting points. It has long been our interest to expand the field of new ionic liquid species upon similarly shaped heterocyclic platforms. The chemistry of substituted 1,2,3-triazolium [9-15] and 1,2,4-triazolium [16-22] salts has been studied extensively, however no attempts have been made preparing ionic liquids based on 1-amino-1,2,3-triazole. We have prepared numerous ionic liquids based on quarternary salts of 4-amino-1,2,4-triazole,[23] as well as a novel class of low melting quarternary salts based upon 1-amino-3-alkyl-1,2,3-triazolium halides.[24] By exchanging the halide for the nitrate anion, which proceeds smoothly and in very high yield, we have prepared a novel class of ionic liquids based upon 1-amino-3-alkyl-1,2,3-triazolum nitrates. The syntheses, physical properties and spectra of all the new compounds, as well as a single crystal x-ray diffraction study will be discussed.

Experimental Section

Methods. Infrared spectra were recorded as KBr discs (using KBr discs as a reference background) on a Nicolet 55XC FT-IR from 4000-400 cm^{-1}. Raman spectra were recorded in pyrex melting point capillaries on Bruker Model FRA 106/S Equinox 55 Raman spectrometer equipped with a 1.06 micron IR excitation laser. NMR experiments were carried out by dissolving the salts in deuterated dimethylsulfoxide in 5 mm NMR tubes, and ^{1}H and ^{13}C spectra recorded on a Bruker Spectrospin DRX 400 MHz

Ultrashield™ NMR. Residual silver and halogen analyses were carried out on a ThermoElemental, XSeries ICP-MS (Inductively Coupled Plasma Mass Spectrometry), equipped with ASIC-510 Autosampler. It was calibrated using standard solutions of silver nitrate, sodium chloride, potassium bromide and potassium iodide. Based on the ionic level of the residual silver and halide in the product salts, the calculated amount of either the corresponding 1-amino-3-alkyl-1,2,3-triazolium halide or silver nitrate was added to the product salt resulting in a purer 1-amino-3-alkyl-1,2,3-triazolium nitrate. Moisture analyses were carried out using EM Science AquaStar® C 3000 titrator, using AquaStar® solution. N-propanol (821.3 ppm) was used as a solvent to determine water levels in products. The single crystal X-ray diffraction data were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (charge coupled device) detector with the χ-axis fixed at 54.74° and using MoK_{α} radiation (λ = 0.71073 Å) from a fine-focus tube. This diffractometer was equipped with KryoFlex apparatus for low temperature data collection using controlled liquid nitrogen boil off. Thermal analyses were carried out in sealed, coated aluminum pans on a Thermal Analyst 2000, Dupont Instruments 910 Differential Scanning Calorimeter. Samples were prepared and sealed inside a nitrogen-filled glove box, and once the pans were inside the DSC cell, the cell was flushed with nitrogen (10 mL per minute) during heating cycles. Elemental analyses were carried out in-house on a Perkin-Elmer Series II 2400 CHNS/O elemental analysis instrument, equipped with AD6 Auto balance and by Desert Analytics, Inc of Tucson, AZ.

Materials. Silver nitrate (99+%), potassium bromide (99%), potassium iodide (99%) was purchased from Aldrich Chemical Company and used without any additional purification. A standard solution (1000 ppm) of sodium chloride was purchased from VWR Scientific. Methanol (99.93%, HPLC grade), acetonitrile (99.93%, HPLC grade), 1-propanol (99.7%) were purchased from Aldrich Chemical Company and used without any additional purification. Diethyl ether was dried through preactivated alumina column prior to use. 1-amino-3-methyl-1,2,3-triazolium iodide, 1-amino-3-ethyl-1,2,3-triazolium bromide, 1-amino-3-n-propyl-1,2,3-triazolium bromide, 1-amino-3-(2-propenyl)-1,2,3-triazolium bromide, 1-amino-3-n-butyl-1,2,3-triazolium bromide were described previously.[24]

1-amino-3-methyl-1,2,3-triazolium nitrate (1a) In a 100 ml flask 1-amino-3-methyl-1,2,3-triazolium iodide (0.5698 g., 2.5 mmoles) was dissolved in 20 ml of methanol at 20°C . A solution of silver nitrate (0.4286 g., 2.5 mmoles) in 30 ml of methanol was added over 15 minutes, under vigorous stirring in the darkness. Silver iodide immediately precipitated. The reaction was stirred for an additional hour, filtered though a Celite plug and washed on filter with an additional 30 ml of methanol. A small aliquot of the mother liquor was heated at 50°C under high vacuum removing all volatiles, weighed and tested for residual silver cations and halide, using ISP-MS methodology. The initial residual silver was measured at 12,970 ppm and iodide at 0.023 ppm, and it was calculated that the product contained 0.0034 g of unreacted silver nitrate. An additional amount of 1-amino-3-methyl-1,2,3-triazolium iodide (0.0046 g) was added to the reaction mixture, and the subsequent reaction mixture filtered, the methanol was distilled off under high

vacuum. The resultant salt was heated to 50°C under high vacuum for 10 hours with frequent agitation, until the vapor pressure was <2×10^{-3} torr, resulting in a high yield 0.3830 g (95%) of 1-amino-3-methyl-1,2,3-triazolium nitrate (mp 86-88°C) DSC onset 185°C; residual silver 4.03 ppm, iodide 1.06 ppm, water 98.5 ppm level. ^{1}H nmr (DMSO-d_6) : d 4.2 (s, 3H), 8.3 (s, 2H), 8.6 (s, 1H), 8.8 (s, 1H). ^{13}C nmr (DMSO-d_6): d 39.6 (s), 126.9 (s), 131.6 (s). Anal. Calcd. for $C_3H_7N_5O_3$: C, 22.22; H, 4.58; N, 43.19. Found: C, 22.18 H, 4.47 ; N, 42.68

1-amino-3-ethyl-1,2,3-triazolium nitrate (1b) Using a manner similar to that for the 1-amino-3-methyl-1,2,3-triazolium iodide cited above, 1-amino-3-ethyl-1,2,3-triazolium bromide (1.8433 g., 9.5 mmoles) was reacted with silver nitrate (1.6206 g., 9.5 mmoles), resulting in a excellent yield 1.6318 g (98 %) of 1-amino-3-ethyl-1,2,3-triazolium nitrate (**1b**), mp 30-32°C; DSC onset 165°C; Initial silver cation level 5,887.4 ppm, bromide 0.0108 ppm, was treated with 1-amino-3-ethyl-1,2,3-triazolium bromide (0.0047 g) residual silver 205 ppm, bromide 32 ppm, water 103.3 ppm. ^{1}H nmr (DMSO-d_6): d 1.5 (m, 3H), 4.5 (m, 2H), 8.3 (s, 2H), 8.6(s, 1H), 8.9 (s, 1H); ^{13}C nmr (DMSO-d_6): d 14.5 (s), 49.1 (s), 127.7 (s), 130.6 (s) Anal. Calcd. for $C_4H_9N_5O_3$: C, 27.43; H, 5.17; N, 39.98. Found: C, 27.39; H, 5.47; N, 39.39.

1-amino-3-n-propyl-1,2,3-triazolium nitrate (1c) Using the same route as above 1-amino-3-n-propyl-1,2,3-triazolium bromide (0.6044 g, 2.9 mmoles) was reacted with silver nitrate (0.4954 g., 2.9 mmoles) resulting in an excellent yield 0.5485 gm (99%) of 1-amino-3-n-propyl-1,2,3-triazolium nitrate **1c**, mp 33-35°C; DSC onset 165°C; final silver level 27 ppm, and bromide 0.595 ppm, water 119.4 ppm. ^{1}H nmr (DMSO-d_6): d 0.9 (t, 3H), 1.9 (m, 2H), 4.5 (t, 2H), 8.3 (s, 2H), 8.7 (s, 1H), 8.9 (s, 1H); ^{13}C nmr (DMSO-d_6):

d 10.4(s), 22.3(s), 54.4(s), 127.18(s), 130.7(s). Anal. Calcd. for $C_5H_{11}N_5O_3$: C, 31.34; H, 5.86; N, 37.02. Found: C, 31.20; H, 6.01; N, 36.62.

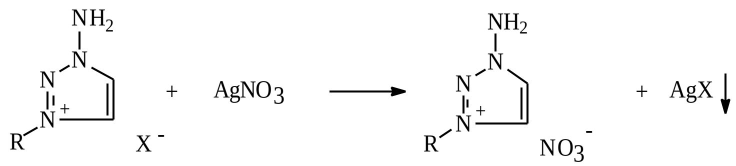
1-amino-3-(2-propenyl)-1,2,3-triazolium nitrate (1d) Using the same method, 1-amino-3-(2-propenyl)-1,2,3-triazolium bromide (3.0543 g, 14.9 mmoles) was reacted with silver nitrate (2.5542 g, 14.9 mmoles) resulting in excellent yield 2.7104 g (99%) of 1-amino-3-(2-propenyl)-1,2,3-triazolium nitrate (**1d**), mp 8-11°C; DSC onset 135°C; silver cation level 1.74 ppm, bromide 0.022 ppm, water 263 ppm. ^{1}H nmr (DMSO-d_6): d 5.2 (d, 2H), 5.4 (t, 2H), 6.0 (m, 1H), 8.4(s, 2H), 8.7 (s, 1H), 8.9(s, 1H); ^{13}C nmr (DMSO-d_6): d 54.9(s), 121.7(s), 127.2(s), 130.3(s), 130.9(s). Anal. Calcd. for $C_5H_9N_5O_3$ (**1d**): C, 32.08; H, 4.84; N, 37.41.Found: C,31.70; H,4.82; N,37.59.

1-amino-3-n-butyl-1,2,3-triazolium nitrate (**1e**) Using the same route, 1-amino-3-n-butyl-1,2,3-triazolium bromide (3.357 g, 15.2 mmoles) was reacted with 2.6545 g (15.2 mmoles) of silver nitrate resulting in excellent yield 3.0765 gm (99%) of 1-amino-3-butyl-1,2,3-triazolium nitrate (**1e**), mp 48-50°C DCS onset 175°C; Initial silver cation level 9,828.2 ppm, bromide 0.017 ppm. treated with 1-amino-3-butyl-1,2,3-triazolium bromide (0.0078 g) resulting in a product with residual silver of 1.8 ppm, and bromide of 105.5 ppm, water 58 ppm. ^{1}H nmr (DMSO-d_6): d 0.9 (m, 3H), 1.3 (m, 2H), 1.8 (m, 2H), 4.6 (m, 2H), 8.3(s, 2H), 8.7 (s, 1H), 8.9 (s, 1H); ^{13}C nmr (DMSO-d_6): d 13.2(s), 18.8(s), 30.7(s), 52.7(s), 127.1(s), 130.7(s). Anal. Calcd. for $C_6H_{13}N_5O_3$: C, 35.46; H, 6.44; N, 34.46. Found: C, 34.92; H, 6.16; N, 34.60.

Results and Discussion.

The general procedure of metathesis comprises the reaction of silver nitrate and the corresponding 1-amino-3-alkyl-1,2,3-triazolium halide in a polar solvent, produces the desired 1-amino-3-alkyl-1,2,3-triazolium nitrates (**1a-e**) with easily separated silver halide in excellent yields (Scheme 1).

Scheme 1. Preparation of 1-amino-3-alkyl-1,2,3-triazolium nitrates (**1a-e**)



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Where R = methyl (**1a**), ethyl (**1b**), n-propyl (**1c**), allyl (**1d**), n-butyl (**1e**) and

X= I^- (**1a**), Br^- (**1b-e**)

Filtration and subsequent solvent removal isolates virtually quantitative yields of highly pure 1-amino-3-alkyl-1,2,3-triazolium nitrates. Methanol was chosen as a reaction media, because it easily dissolves all the starting materials and ease of removal after reaction completion. Several leaders in the area of ionic liquids have stressed the issue of contamination of ionic liquids, specifically by water, residual metals cations and halide anions.[1-3,7] All products were isolated and manipulated using Schlenk flasks in a dry box, under nitrogen atmosphere, and careful precautions taken to exclude any contact with air. To prevent the contamination of the products by elemental silver, reactions were carried out in the darkness. After the reactions were completed, the product solutions were tested for residual silver cations and halides using ICP-MS analyses quantifying the amount of

contaminants. The level of contamination by silver cations or halide anions was detected in the 0.003-1.0% region. Calculated amounts of the corresponding 1-amino-3-alkyl-1,2,3-triazolium halides were then added to their initial product salt to further purify the product salts. This method was sufficient enough to remove greater then 99.99% of these contaminants, without sacrificing the yield. After the level of residual silver and halides was $\leq$100 ppm, materials were considered pure enough to study their spectral and physical properties. Residual silver in **1b** was detected on the slightly higher level of 205 ppm. Minimal error in weighing of either reagent undoubtedly results in trading a silver cation contamination for halide contamination, which was found to be the case in **1e**. The water level was determined by Karl-Fisher titration method, where **1a** was analyzed directly as a solid, while **1b-e** (viscous liquids) were analyzed as solutions in 1-propanol. The water level in 1-propanol was found to be 821.3 ppm. Pre-weighed samples of **1b-e** sealed in HPLC sample vials, were dissolved in 1-propanol (about 350 mg in 2 ml of 1-propanol) and these solutions were injected by syringe into the Karl-Fisher titrator and analyzed for water. The water content in **1b-e** was calculated using the titration data and concentration of **1b-e** in 1-propanol and found to be on 50-250 ppm level.

The vibrational spectra of all the 1-amino-3-alkyl-1,2,3-triazolium nitrates (**1 a-e**) revealed evidence of N-alkylation of the 1,2,3-heterocyclic ring, however the peaks are overlapping and assignments are difficult in this region. Peaks in the area of 3200-3100 cm^{-1} typically assigned to NH_2 stretching modes.[22-24] Sharp, but complex peaks are present in area of 3100-2900 cm^{-1}, typical of both heterocyclic C-H and alkyl C-H stretching modes, and as the pendant alkyl chain is lengthened, these peaks grow increasingly complex. The presence of a broad, intense band in the area 3300-2600 cm^{-1}

is strong evidence of complex hydrogen bonding, involving N-H and C-H protons as well $NH_2 \ldots X^-$, interactions. These are not unusual and have been observed in several other nitrogen based salt systems.[22-27] An intense absorption indicative of the free nitrate anion is present in the vibrational spectra for all compounds in the area of 1350-1360 cm^{-1} (IR) and at 1043 cm^{-1} (Raman), which is typical and have been observed in other nitrate salts.[22,23, 28-30]

The proton nmr spectra of the triazolium nitrates showed strong evidence of ring nitrogen alkylation, with downfield shifts (averaging 1.0 ppm) observed in the signals of the C-H protons of the heterocyclic ring as compared to the neutral heterocycle 1-amino-1,2,3-triazole.[24] The pendant N-amino protons are shifted downfield an average of 1.4 ppm as compared to the neutral 1-amino-1,2,3-triazole. These shifts can most likely be attributed to the formal (+1) charge placed upon the alkylated N(3) atom of the 1,2,3-triazole ring reducing the overall electron density of the ring, effectively deshielding all the respective hydrogen environments.

In the ^{13}C spectra slight downfield shifts (averaging 1.0-2.0 ppm) are observed in the heterocyclic carbon signals as compared to neutral 1-amino-1,2,3-triazole.[24] The formation of a cationic species, is most likely responsible for these shifts, has been noted before in other alkylated triazole systems.[31-36] ^{1}H and ^{13}C nmr shifts of the ring and pendant alkyl groups are virtually identical to those observed in the corresponding 1-amino-3-alkyl-triazolium halides.[24]

As been noted for the 1-alkyl-4-amino-1,2,4-triazolum, the nitrates have lower melting points then their corresponding halide precursors.[23] Paralleling this trend, the 1-amino-3-alkyl-1,2,3-triazolum nitrates have substantially lower melting points then their

halide parents and meet the well accepted definition of an ionic liquid[1-4] (Table 1). 1-amino-3-methyl-1,2,3-triazolium (**1a**) nitrate was isolated as a colorless crystals, the other salts **1b-e** were isolated as viscous ionic liquids, which eventually solidify upon standing, except for 1-amino-3(2-propenyl)-1,2,3-triazolium nitrate (**1d**). In order to determine the actual melting point for most of the new salts, which were initially recovered as supercooled viscous liquids, they were subjected to cycles of fast cooling using liquid nitrogen to -100 to -80°C, followed by heating (10°C per minute) to 70-80°C. During several cycles of cooling and heating, detection of reproducible melting points was found for the **1b-d**. For the ethyl (**1b**) and allyl (**1d**) salts, crystallization was observed with exotherms observed at -24°C and -8°C respectively prior to their melting endotherms.

Table 1. Melting points and DSC onsets of 1-amino-3-alkyl-triazolium nitrates (**1a-e**)

compounds	melting point	DSC onset
1-amino-3-methyl-1,2,3-triazolium nitrate (**1a**)	86-88°C	185°C
1-amino-3-ethyl-1,2,3-triazolium nitrate (**1b**)	30-32°C [a]	165°C
1-amino-3-propyl-1,2,3-triazolium nitrate (**1c**)	33-35°C	165°C
1-amino-3-(1)propenyl-1,2,3-triazolium nitrate (**1d**)	8-11°C [b]	135°C
1-amino-3-butyl-1,2,3-triazolium nitrate (**1e**)	48-50°C	175°C

(a) Reversible exothermic crystalline phase change at -27- (-21)°C

(b) Reversible exothermic crystalline phase change at -10°C prior to the melting point.

All the new salts were highly soluble in polar solvents such as water, methanol, ethanol, dimethylformamide, dimethylsulfoxide, acetonitrile and insoluble in chloroform,

diethyl ether, and tetrahydrofuran. All the new materials melt well below 100°C, while retaining a reasonably long liquidous range before DSC onset, defining them as new members of the well known class of ionic liquids.

Single crystal studies

Interest in substituted 1,2,3-triazoles, fueled by pharmaceutical efforts [37-40] and their use in industrial applications,[41] has resulted in numerous crystallographic studies, however, information is available mostly for 4,5-substituted-1,2,3-triazoles [42-48] or annulated compounds.[49-56] In our previous publication, we reported crystal structures of 1-amino-3-methyl-1,2,3-triazolium iodide along with several other 1-amino-3-alkyl-1,2,3-triazolium bromides.[24] In the present study we undertook a single crystal x-ray crystallography study on 1-amino-3-methyl-1,2,3-triazolium nitrate (**1a**), verifying its structure, as well as investigating the effects of the NO_3^- anion. The structure was compared to previously reported 1-amino-3-methyl-1,2,3-triazolium iodide salt as well as the neutral heterocycle 1-amino-1,2,3-triazole.[24]

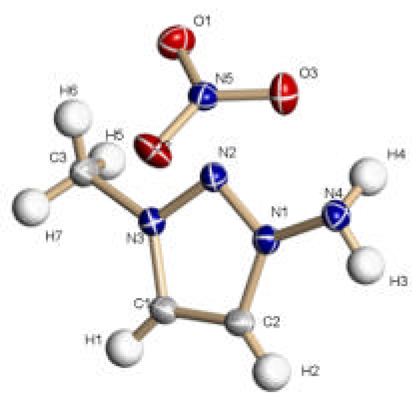
1-amino-3-methyl-1,2,3-triazolium nitrate (**1a**) crystallized in an orthorhombic crystal system with Pbca space group symmetry with the asymmetric cation and anion shown in Figure 1 and details of the x-ray study are summarized in Table 2.

Table 2. Crystal Data for 1-amino-3-methyl-1.2.3-triazolium nitrate (**1a)**

Formula	C3 H7 N5 O3
Formula Weight	161.14
Crystal System	Orthorhombic
Space group	Pbca (No. 61)

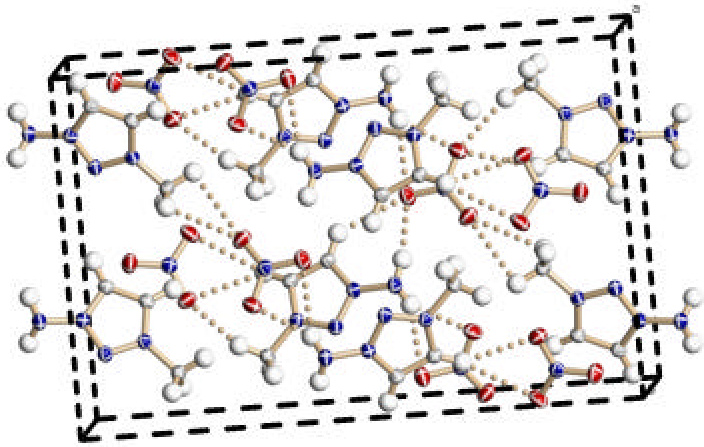
Unit cell dimensions [Å] and angles (°)	
a	6.427(1)
b	11.540(2)
c	17.870(3)
a	90
ß	90
?	90
Volume [Å^3]	1325.4(4)
Z	8
Density (calc) [g/cm^3]	1.615
µ(MoKa) [/mm]	0.141
F(000)	672
Crystal Size [mm]	0.34 x 0.320 x 0.11
<u>Data Collection</u>	
Temperature (K)	100
Radiation [Angstrom]	MoKa 0.71073
T Min-Max [°]	2.3, 28.2
Dataset h,k,l	-8: 8 ; -15: 15; -22: 23
Tot., Uniq. Data, R(int)	13989, 16.28, 0.026
Observed data [I > 2.0 s(I)]	1559
<u>Refinement</u>	
Nref, Npar	1628, 128
R, wR2, S	0.0404, 0.0959, 1.15
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å^3]	-0.24, 0.28

Figure 1. Crystal structure of 1-amino-3-methyl-1,2,3-triazolium nitrate (**1a)**



As expected the structural analysis confirmed quarternization of nitrogen atom (3) in the 1,2,3-triazole ring. There is a single nitrate anion per 1-amino-3-methyl-1,2,3-triazolium cation as expected. Bond distances between carbon and nitrogen atoms of the 1,2,3-triazole ring (C(1)-N(3) = 1.344(2) Å and C(2)-N(1) = 1.349(2) Å) are longer than the expected values for a typical C-N double bond (1.265 Å), but shorter than a typical C-N single bond (1.470 Å) [57], supporting delocalization of electron density throughout the 1,2,3-triazole ring. This has been observed in many other 1,2,3-triazole systems.[42-54] A striking difference of the nitrate salt versus the iodide salt is the orientation of the pendant N-NH_2 group in 1-amino-3-methyl-1,2,3-triazolium nitrate. The N-amino protons are on the same side of the imaginary plane passing through the C and N atoms of the cation. In 1-amino-3-methyl-1,2,3-triazolium iodide, the N(4)-H(4) bond of the pendant amino group is in the plane of the 1,2,3-triazolie ring.[24] Some changes in bond distances in pendant N-amino group, thus (N(4) – H(4) = 0.87 (2) Å) is slightly longer, as corresponding bond in 1-amino-3-methyl-1,2,3-triazolium iodide, which (N(4) – H(4) = 0.81 (3) Å) [24] . This increase of N(4)-H(4) bond distance most likely may be attributed proton H(4) being involved in hydrogen bond interactions with the two corresponding oxygen atoms of nitrate anion (H(4)…O(1) = 2.11(3) Å and H(4)…O(2) = 2.50(2) Å (Figure 2, Table 4). Nevertheless, C-H and N-H bond distances are essentially identical to those observed in the iodide salt and require no further discussion.

Figure 2. Some of significant cation-anion hydrogen bond contacts in 1-amino-3-methyl-1,2,3-triazolium nitrate (**1a**).



Proton H(3) of the pendant amino group is involved in strong hydrogen bond interactions with two oxygen atoms of the nitrate anion (H(4)…O(1) = 2.46(2) Å and H(4)…O(1) = 2.21(2) Å (Figure 3, Table 4). As well strong hydrogen bond interactions of the H(3) and H(4) protons (Figure 3, Table 4) of the pendant amino group, resulting in both N(4)-H(3) and N(4)-H(4) bonds being on one side of the 1,2,3-triazole ring, and forcing the lone pair out the plane of the ring. Both C-H protons of the 1,2,3-triazole ring are involved in the hydrogen bonding with oxygen atoms of the nitrate anion, there H(1) proton forms two hydrogen bonds (H(1)…O(2) = 2.67(2) Å, H(1)…O(3) = 2.59(2) Å) and H(2) proton form one hydrogen bond (H(2)…O(1) = 2.53(2) Å) with the corresponding oxygen atom of the nitrate anion. These interactions are well within Van der Waal[57] distances and have been observed in other N-NH_2 heterocyclic cation systems.[58-60] It is worth noting the slight difference in the N-O bond distances in the nitrate anion (Table 3), thus N(5)-O(1) = 1.259(2) Å is slightly longer then the N(5)-O(2) = 1.244(2) Å and N(5)-O(3) = 1.249(2) Å. All the oxygen atoms of nitrate anion form multiple hydrogen bonds with the

corresponding protons of the N-amino group, the C-H protons of the 1,2,3-triazole ring as well as protons of the pendant methyl group of the same or another cation. However only oxygen atom O(1) of the nitrate anion is involved in strong interactions (O(1)c…H(3)-N(4) = 2.11(2) Å, O(1)d…H(4)-N(4) = 2.46(2) Å) (Figure 3, Table 4) with protons of two different amino-groups, which is likely responsible for the difference in bond distances of the nitrate anion.

Table 3. Interatomic bond distances [Å] in 1-amino-3-methyl-1,2,3-triazolium nitrate (**1a**)

O(1) - N(5)	1.259(2)	N(4) - H(4)	0.87(2)
O(2) - N(5)	1.244(2)	N(4) - H(3)	0.88(2)
O(3) - N(5)	1.249(2)	C(1) - C(2)	1.367(2)
N(1) - C(2)	1.349(2)	C(1) - H(1)	0.95(2)
N(1) - N(4)	1.393(2)	C(2) - H(2)	0.93(2)
N(1) - N(2)	1.316(2)	C(3) - H(5)	0.98 2)
N(2) - N(3)	1.326(3)	C(3) - H(6)	0.94(2)
N(3) - C(1)	1.344(2)	C(3) - H(7)	0.96(2)
N(3) - C(3)	1.465(2)		

Table 4. Significant cation-anion contacts lengths [Å], angles [°] and their symmetry code in **1a**.

O(1)c…H(3) - N(4)	2.11(2)	168(2)	0.88(2)	½-x, 1-y, -½+z
O(2)c…H(3) - N(4)	2.50(2)	135(2)	0.88(2)	½-x, 1-y, -½+z
O(1)d…H(4) - N(4)	2.46(2)	152(2)	0.87(2)	x, ½-y, -½+z
O(3)d…H(4) - N(4)	2.21(2)	153(2)	0.87(2)	x, ½-y, -½+z
O(2)…. H(1) - C(1)	2.67(2)	136(1)	0.95(2)	x, y, z
O(3)…. H(1) - C(1)	2.59(2)	136(2)	0.95(2)	x, y, z
O(1)c…H(2) - C(2)	2.53(2)	134(2)	0.93(2)	½-x, 1-y, -½+z
O(3)…. H(7) - C(3)	2.30(2)	149(2)	0.96(2)	x, y, z

Conclusion.

A novel class of ionic liquids based upon 1-amino-3-alkyl-1,2,3-triazolium nitrates have been synthesized and characterized using mass balance, multinuclear nmr, DSC, vibrational spectroscopy, and contaminant levels of silver, halides and water. The melting points of these materials are substantially lower then the corresponding halides, and further substantiate the correlation of charge delocalization in the anion lowering the melting point of the ionic liquid. A convenient method was used for determining halide and silver contaminants in the ionic liquids. The product salts were diluted with water and analyzed on an ICP-MS instrument. Prior to the analyses, standard diluted solutions of the representative ion were made, resulting in a reproducible detection curve. Upon analysis of a nitrate salt, the total amount of either un-reacted starting halide or over-added silver nitrate was calculated, whereupon re-addition of the appropriate starting material was carried out in order to reduce the contaminant in issue to $\leq$100 ppm upon further analysis. A single crystal x-ray diffraction study of the 1-amino-3-methyl-1,2,3-triazolium nitrate, revealed a change in the orientation of the N-amino group, differing from 1-amino-3-methyl-1,2,3-triazolium iodide. Strong hydrogen bonding interactions are likely responsible for the N-amino group orientation and in the bond lengths of the nitrate anion in the 1-amino-3-methyl-1,2,3-triazolium nitrate.

Acknowledgments

The authors would like to thank Michael Berman (AFOSR) and Michael Huggins (AFRL/PRS), Ronald Channell (AFRL/PRSP) and Wayne Kalliomaa (AFRL/PRSP) for financial support and encouragement of this work

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